

have been found it; so that as in the case of Spiti and other areas its exact age cannot be known; the only limits being Upper Silurian below and Lower Carboniferous above. It may therefore be of either of these ages, or it may be Devonian, or represent any two or all three of them".

The fossils now found are well preserved and occur in profusion though extraction is difficult. We have identified the trilobite *Phacops rana* Green; the brachiopods *Athyris spiriferoides* (Eaton), *Meristella atoka* Girty, and *Spirifer* sp.; a gastropod as *Diaphorostoma* sp. and a lamelibranch as *Modiolomorpha* sp. This fauna indicates a Devonian age—thus proving the age of a part at least of the Quartzite.

Further work is in progress on both the new Silurian and Devonian faunas. *Note added in proof.* We have now learned that I. Strachan, J. W. A. Bodenhausen, T. de Booy and C. G. Egeler have announced (*Geol. en Mijnb.*, 43, 380; 1964) the finding of early Silurian graptolites in Nepal.

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## CRYSTALLOGRAPHY

### Electron Diffraction Study of Evaporated Beryllia

WHEN beryllia flakes, supported on thin carbon films to form electron microscope specimens, are strongly irradiated with an electron beam, they disintegrate and small crystals condense on the surrounding carbon film. Willis, Austerman and Dearborn<sup>1</sup> reported that the condensed material gives electron diffraction ring patterns which they identify as being those of the high-temperature  $\beta$ -BeO phase examined by Smith, Cline and Frechette<sup>2</sup>. These latter authors suggest that the  $\beta$ -phase is cubic,  $a_0 = 4.76 \text{ \AA}$ , with a non-trivial structure. According to Austerman<sup>3</sup>, more recent work has suggested that the structure may be hexagonal or tetragonal.

The ring patterns of Willis *et al.* contain rings attributable to both the  $\beta$ -phase and the low-temperature  $\alpha$ -phase. The absence of the (002) ring on  $\alpha$ -BeO could be assumed to result from preferred orientations of the crystals.

In the course of an investigation of the disintegration of BeO crystals under electron irradiation in our *JEM-6A* electron microscope we have made observations on the crystals condensed on the supporting film which parallel those of Willis *et al.* However, we have found that under certain ill-defined conditions of electron irradiation, the condensed crystals take the form of comparatively large, thin crystal plates (linear dimensions of a few thousand  $\text{\AA}$ ) from which we have obtained fragmentary single-crystal patterns by selected-area diffraction methods.

From some areas we have obtained almost complete rotation patterns, given by a crystal or a set of parallel crystals bent around one axis.

Interpretation of these patterns shows clearly that the predominating ring pattern comes from a single substance rather than from a mixture of the  $\alpha$  and  $\beta$  phases. The rotation pattern is readily interpreted in terms of a hexagonal unit cell with  $a_0 = 5.40 \text{ \AA}$  and  $c_0 = 4.62 \text{ \AA}$ , the

accuracy of determination being in each case about 0.5 per cent. The rotation is about the  $c$ -axis. On the zero layer line,  $l = 0$ , the  $hk0$  arcs are present only for both  $h$  and  $k$  even. The same may apply for  $l = 2n$  because weak spots with  $h$  or  $k$  odd on layer lines with  $l = \pm 2$  may be due to secondary scattering. Because the  $a$  dimension is very close on twice that for  $\alpha$ -BeO (2.70  $\text{\AA}$ ) and the  $c$ -dimension is very nearly equal to the (100) spacing (4.68  $\text{\AA}$ ) the principal  $\alpha$ -BeO rings appear to be present in the ring patterns (apart from the 002), and the rings not attributable to  $\alpha$ -BeO have radii showing simple arithmetic relationships which could suggest a cubic structure.

The relationship between this hexagonal phase and the high-temperature  $\beta$ -BeO phase of Smith *et al.* remains obscure. The strong preferred orientation thought to be present in the high-temperature phase could possibly limit the pattern of the hexagonal phase to lines which could be indexed as cubic, and the report that the high-temperature phase could be hexagonal is suggestive. An identification of this sort would remove doubts that the observed hexagonal phase is actually BeO, since the possibility must be considered that it results from reaction of the BeO with the gases present or the carbon supporting film.

The existence of a structure derived from  $\alpha$ -BeO with commensurate unit cell dimensions (except for a 6 per cent increase in  $c$ -axis) is of particular interest in relation to the anisotropic expansion of the lattice of BeO irradiated in a nuclear reactor at moderate temperature<sup>4</sup>. The relatively great expansion in the  $c$ -direction commonly observed could be explained if a primary effect of irradiation was the formation of small nuclei of this hexagonal phase.

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## METALLURGY

### Effect of Grain Boundaries on the Diffusional Growth of Oxides on Metals

SEVERAL mechanisms<sup>1-3</sup> for the growth of thin films of oxides on metals have yielded equations of the form  $y^3 = kt$ , where  $y$  is the film thickness,  $k$  a rate constant, and  $t$ , time. However, none of these mechanisms can be satisfactorily extended to the case of thick films formed on such metals as titanium, zirconium and tantalum<sup>4</sup>. It is proposed that this so-called 'cubic' oxidation can result from a combination of diffusion along grain boundaries and normal bulk diffusion in relatively thick oxide films.

The usual high-temperature protective oxidation of metals obeys a parabolic kinetic law,  $y^2 = k't$ , and the mechanism universally accepted for this law is that proposed by Wagner<sup>5</sup>. The oxide is assumed to grow by the diffusion of defects across the film. Constant defect concentrations at the metal-oxide and oxide-gas interfaces provide a gradient of chemical potential inversely proportional to film thickness. It is assumed in this mechanism that diffusion occurs across the bulk of the oxide film and that grain boundaries in the oxide film can be safely ignored.

In laboratory determinations of diffusion coefficients the possibility of grain boundary effects, especially at moderate temperatures, is generally appreciated<sup>6</sup>. The significance of grain boundary effects can be examined by